

# PRODUCTION OF REINFORCED POLYBUTADIENE RUBBER

**Publication number:** JP58109513 (A)

**Publication date:** 1983-06-29

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**Classification:**






**- international:** C08F4/00; C08F4/60; C08F6/00; C08F6/06; C08F6/10;  
C08F36/00; C08F136/06; C08F236/00; C08F295/00; C08F4/00;  
C08F6/00; C08F36/00; C08F136/00; C08F236/00; C08F295/00;  
(IPC1-7): C08F4/52; C08F6/10; C08F136/06

**- European:** C08F136/06; C08F295/00

**Application number:** JP19810208108 19811224

**Priority number(s):** JP19810208108 19811224

**Also published**

 JP63036324  
 JP1488622  
 FR2519008 (  
 US4476287  
 GB2114582

more

## Abstract of JP 58109513 (A)

**PURPOSE:** To obtain efficiently the titled rubber with excellent physical properties, by dissolving 1,3-butadiene in an inert organic solvent, subjecting the solution to a 1,4-polymerization reaction in the presence of a cis-1,4-polymerization catalyst and subjecting the mixture to a 1,2-polymerization reaction after the addition of a specified 1,2-polymerization catalyst. **CONSTITUTION:** 1,3-Butadiene is dissolved in an inert organic solvent. The solution is further mixed with an organoaluminum compound of formula I, wherein R is a 1-6C alkyl, phenyl, or cycloalkyl, and a cobalt compound which constitute a cis-1,4-polymerization catalyst, and subjected to a 1,4-polymerization.; After the addition of a 1,2-polymerization catalyst obtained from an organoaluminum compound of formula II and carbon disulfide, the reaction mixture is subjected to a 1,2-polymerization reaction to form the purpose polybutadiene rubber consisting of 5-30wt% boiling n-hexane-insoluble portion and 95-70wt% soluble portion. Then, the unreacted 1,3-butadiene and the inert organic solvent are distilled, recovered and recirculated.

AC R<sub>2</sub> X

AC R<sub>2</sub>

# United States Patent [19]

Maehara et al.

[11] Patent Number: 4,476,287

[45] Date of Patent: Oct. 9, 1984

[54] **PROCESS FOR PRODUCING  
POLYBUTADIENE RUBBER WITH  
ENHANCED MECHANICAL STRENGTH**

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[21] Appl. No.: 448,232

[22] Filed: Dec. 9, 1982

[30] **Foreign Application Priority Data**

Dec. 24, 1981 [JP] Japan ..... 56-208108

[51] Int. Cl.<sup>3</sup> ..... C08F 4/26

[52] U.S. Cl. .... 526/92; 526/140

[58] Field of Search ..... 526/66, 92; 525/247,  
525/53

[56] **References Cited**

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[57] **ABSTRACT**

A polybutadiene rubber having an enhanced mechani-

cal strength is produced in such a manner that the content of water in a solution of 1,3-butadiene in an inert organic solvent is controlled to 0.2 to 5 millimoles per liter of 1,3-butadiene; a first polymerization mixture is prepared from the controlled 1,3-butadiene solution, an organic aluminum compound of the formula  $AlR_nX_{3-n}$ , wherein  $R=C_{1-6}$  alkyl, phenyl, or cycloalkyl,  $X=$  halogen, and  $n=1.5-2.0$ , and a cobalt compound, for example, by aging a mixture of the controlled 1,3-butadiene solution with the aluminum compound for at least one minute and then by admixing the aged mixture with the cobalt compound; the first polymerization mixture is subjected to a cis-1,4-polymerization; a second polymerization comprising the resultant cis-1,4-polybutadiene, non-reacted 1,3-butadiene, the inert organic solvent, and a catalyst comprising an organic aluminum compound of the formula  $AlR_3$ , a cobalt compound, and carbon disulfide is subjected to a 1,2-polymerization to produce a polybutadiene rubber consisting essentially of 5% to 30% by weight of a boiling n-hexane-insoluble fraction and 70% to 95% by weight of a boiling n-hexane-soluble fraction thereof and having an excellent mechanical strength; and after the 1,2-polymerization is shortstopped, the resultant polybutadiene rubber is isolated from the 1,2-polymerization mixture.

34 Claims, 2 Drawing Figures

Fig. 1

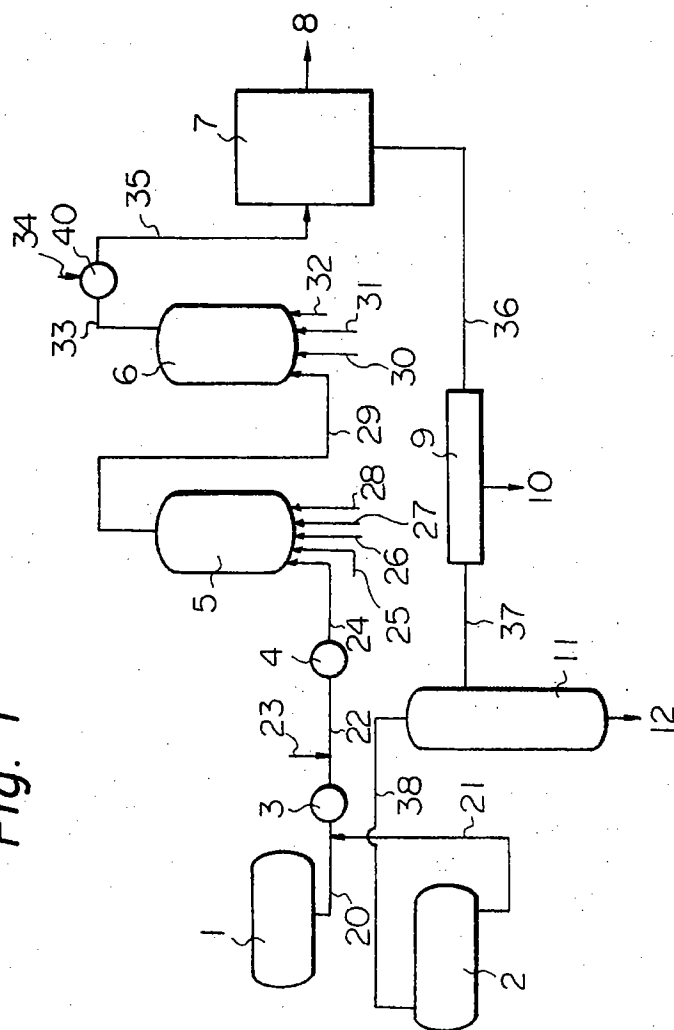
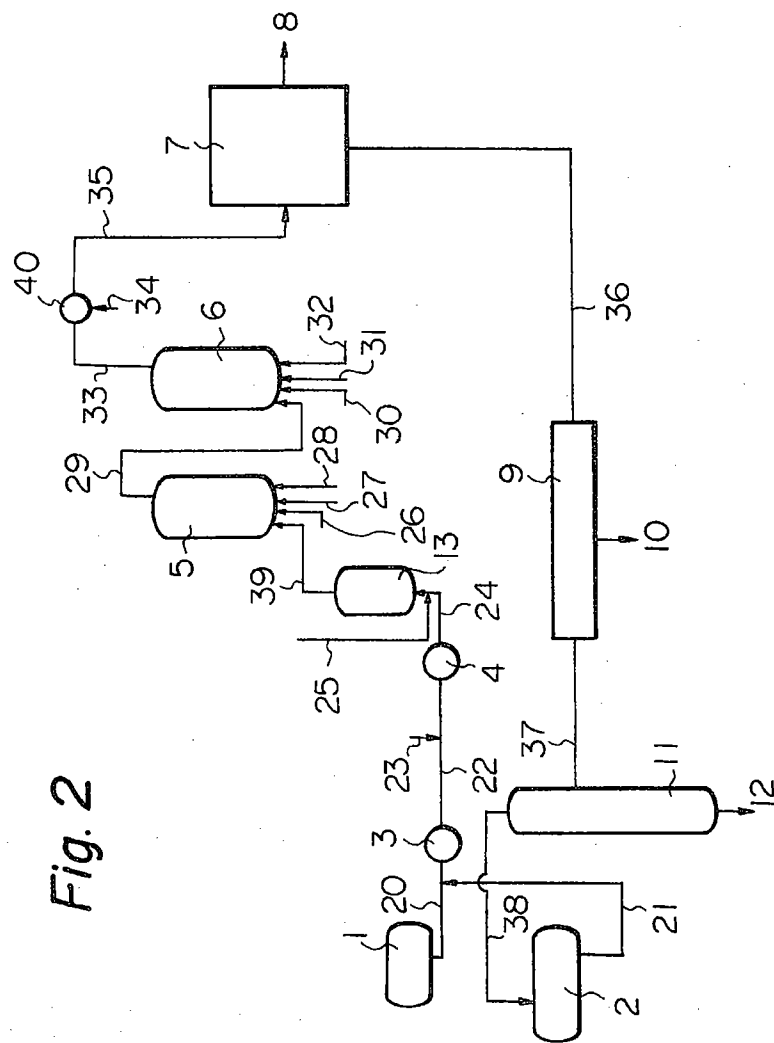


Fig. 2



# PROCESS FOR PRODUCING POLYBUTADIENE RUBBER WITH ENHANCED MECHANICAL STRENGTH

## FIELD OF THE INVENTION

The present invention relates to a process for producing a polybutadiene rubber having an enhanced mechanical strength. More particularly, the present invention relates to a process for producing a polybutadiene rubber comprising 5% to 30% by weight of a fraction insoluble in n-hexane at the boiling temperature thereof and 70% to 95% by weight of a fraction soluble in the boiling n-hexane and having an excellent mechanical strength.

## DESCRIPTION OF THE PRIOR ART

Large amounts of cis-1,4-polybutadiene, produced by polymerizing 1,3-butadiene in the presence of a cis-1,4-polymerization catalyst, are used as materials for tires and other rubber products. One of the reasons why large amounts of cis-1,4-polybutadiene are used in the rubber industry is that the rubber products produced therefrom exhibit high resilience, a low heat buildup, and superior abrasion resistance and, therefore, are superior to general purpose rubber products. Conventional cis-1,4-polybutadiene rubber products, however, suffer from the disadvantages of poor tear resistance and small cut growth resistance.

In order to eliminate the above-mentioned disadvantages of conventional cis-1,4-polybutadiene rubber products, Japanese Examined Patent Publication (Kokoku) No. 49-17666 discloses a new type of polybutadiene rubber produced by first polymerizing 1,3-butadiene in an inert organic solvent in the presence of a cis-1,4-polymerization catalyst and then second polymerizing 1,3-butadiene in the presence of a 1,2-polymerization catalyst. The publication contains some examples of processes in which polybutadiene rubbers are vulcanized and in which the resultant vulcanized rubber products exhibit excellent tear resistance and cut growth resistance.

The above-mentioned process, however, has several disadvantages which have kept it from being utilized in the polybutadiene rubber industry. That is, in the second polymerization procedure, carbon disulfide is used as a catalytic ingredient of the 1,2-polymerization catalyst. After the first and second polymerization procedures are completed, however, the carbon disulfide cannot easily be separated from the non-reacted 1,3-butadiene and the inert organic solvent, especially, from the non-reacted 1,3-butadiene. Also, carbon disulfide causes some undesirable side reactions when contacted with a halogen-containing organic aluminum compound in the absence of water, particularly in the presence of a cobalt compound. Products of such side reactions hinder the polymerization of 1,3-butadiene. Accordingly, it is essential to handle the carbon disulfide very carefully so as to prevent the above-mentioned side reactions.

Under these circumstances, a strong demand exists in the polybutadiene rubber industry for a new process for continuously producing a polybutadiene rubber having enhanced tear resistance and cut growth resistance in addition to excellent impact resilience and abrasion resistance and overcoming the disadvantages incurred with use of carbon disulfide.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing a polybutadiene rubber having enhanced mechanical strength, for example, excellent tear resistance cut growth resistance, and abrasion resistance.

Another object of the present invention is to provide a process for producing a polybutadiene rubber wherein the carbon disulfide used as a catalytic ingredient of the second polymerization catalyst can be easily separated from non-reacted 1,3-butadiene and the inert organic solvent.

The above-mentioned objects can be attained by the process of the present invention which comprises the successive steps of:

(A) mixing 1,3-butadiene with an inert organic solvent to provide a 1,3-butadiene solution;

(B) controlling the concentration of water contained in the 1,3-butadiene solution to from 0.2 to 5 millimoles per liter of the 1,3-butadiene solution;

(C) subjecting a first polymerization mixture, which comprises the controlled 1,3-butadiene solution and a cis-1,4-polymerization catalyst comprising:

(a) an aluminum catalytic ingredient consisting of at least one organic aluminum compound of the formula (I):



wherein R represents a member selected from the group consisting of alkyl radicals having 1 to 6 carbon atoms, a phenyl radical, and cycloalkyl radical; X represents a halogen atom, and n represents the number of 1.5 to 2.0; and

(b) a cobalt catalytic ingredient consisting of at least one cobalt compound, to a cis-1,4-polymerization to convert at least a portion of the 1,3-butadiene contained in the first polymerization mixture to cis-1,4-polybutadiene;

(D) subjecting a second polymerization mixture, which comprises the resultant cis-1,4-polybutadiene, non-reacted 1,3-butadiene, organic solvent, and 1,2-polymerization catalyst comprising:

(c) a cobalt catalytic ingredient consisting of at least one cobalt compound,

(d) an aluminum catalytic ingredient consisting of at least one organic aluminum compound of the formula (II):



wherein R is the same as defined above; and

(e) carbon disulfide, to 1,2-polymerization to provide a polybutadiene rubber consisting essentially of 5% to 30% by weight of a boiling n-hexane-insoluble fraction and 70% to 95% by weight of a boiling n-hexane-soluble fraction thereof;

(E) stopping the 1,2-polymerization by adding a polymerization shortstopper to the resultant second polymerization mixture; and

(F) isolating the resultant polybutadiene rubber from the stopped second polymerization mixture.

In the process of the present invention, the first polymerization mixture may be prepared by mixing the controlled 1,3-butadiene solution of step (B) with the 1,4-polymerization catalyst or may be provided by admixing the controlled 1,3-butadiene solution of step (B)

with the aluminum catalytic ingredient (a) by aging the resultant admixture for at least one minute and, then, by mixing the aged mixture with the cobalt catalytic ingredient (b).

Also, in the process of the present invention, after the resultant polybutadiene is isolated from the stopped second polymerization mixture, the isolation residue can be processed for elimination of the carbon disulfide and for recovery of a mixture of the non-reacted 1,3-butadiene and the inert organic solvent substantially free from carbon disulfide.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow sheet of an example of the process of the present invention in which a first polymerization mixture is prepared by directly mixing a controlled 1,3-butadiene solution with a cis-1,4-polymerization catalyst and in which an inert organic solvent having a boiling point higher than that of 1,3-butadiene is used;

FIG. 2 is a flow sheet of another example of the process of the present invention in which an inert organic solvent having a boiling point higher than that of 1,3-butadiene is used and in which a first polymerization mixture is prepared by aging a mixture of a controlled 1,3-butadiene solution with an aluminum catalytic ingredient and then by mixing the aged mixture with a cobalt catalytic ingredient.

### DETAILED EXPLANATION OF THE INVENTION

In step (A) in the process of the present invention, a 1,3-butadiene solution is prepared by mixing 1,3-butadiene in an inert organic solvent. In this step, it is preferable that the amount of 1,3-butadiene be at least 3%, more preferably, 3% to 40%, based on the sum of the weight of 1,3-butadiene and the inert organic solvent.

The inert organic solvent is not limited to a specific type of liquid compound as long as the solvent is able to dissolve therein the cis-1,4-polybutadiene produced in step (C). Usually, the inert organic solvent consists essentially of at least one member selected from the group consisting of aromatic hydrocarbons, for example, benzene, toluene, and xylene; aliphatic hydrocarbons, for example, n-heptane and n-hexane; cycloaliphatic hydrocarbons, for example, cyclohexane and cyclopentane; and halogenated derivatives of the above-mentioned hydrocarbons, for example, dichloromethane and chlorobenzenes.

In step (B) of the process of the present invention, the concentration of water contained in the 1,3-butadiene solution is controlled to a desired value in the range of from 0.2 to 5 millimole, preferably, from 0.5 to 5 millimoles, per liter of the 1,3-butadiene solution. The control of the water concentration can be effected by any conventional water-controlling method.

A concentration of water in the 1,3-butadiene solution less than 0.2 millimole/l or more than 5 millimoles/l will result in an unsatisfactory yield of cis-1,4-polybutadiene in step (C). If it is found that the concentration of water in the 1,3-butadiene solution prepared in step (A) is the same as that desired, the 1,3-butadiene solution can be directly subjected to step (C). The measurement and control of the water concentration can be carried out by a conventional method. Before the controlled 1,3-butadiene solution is subjected to step (C), it is preferable that the solution be cooled to a temperature of 10° C. or less.

In step (C), a first polymerization mixture comprising the controlled 1,3-butadiene solution and a cis-1,4-polymerization catalyst is subjected to a first polymerization procedure. The cis-1,4-polymerization catalyst comprises (a) an aluminum catalytic ingredient consisting of at least one organic aluminum compound of the formula (I):



wherein R represents a member selected from the group consisting of alkyl radicals having 1 to 6 carbon atoms, a phenyl radical, and cycloalkyl radical, preferably, having 5 to 7 carbon atoms; X represents a halogen atom, preferably, a chlorine atom; and n represents the number of 1.5 to 2.0 and (b) a cobalt catalytic ingredient consisting of at least one cobalt compound which is soluble in the inert organic solvent used for dissolving 1,3-butadiene therein.

The organic aluminum compound of the formula (I) is preferably selected from the group consisting of diethyl aluminum monochloride, diethyl aluminum monobromide, diisobutyl aluminum monochloride, and ethyl aluminum sesquichloride.

The cobalt compounds usable for the cis-1,4-polymerization catalyst are not limited to a specific type of compound as long as the cobalt compounds are soluble in the inert organic solvent contained in the 1,3-butadiene solution. Preferably, the cobalt compound is selected from the group consisting of cobalt-ketone complexes, for example, cobalt (II) acetylacetonate and cobalt (III) acetylacetonate; cobalt-ketoacid ester complexes, for example, cobalt acetacetic ethylester complexes; cobalt salts of organic carboxylic acids having 6 or more carbon atoms, for example, cobalt octoate, cobalt naphthenate, and cobalt benzoate; cobalt halide complexes, for example, cobalt chloride-pyridine complexes and cobalt chloride-ethyl alcohol complexes; and cobalt complexes coordinated with butadiene, for example, (1,3-butadiene) 1-(2-methyl-3-butenyl)- $\pi$ -allyl-cobalt which complexes are prepared by mixing cobalt compounds with an organic aluminum compound, organic lithium compound or alkyl magnesium compound and 1,3-butadiene.

The first polymerization mixture can be prepared by mixing the controlled 1,3-butadiene solution with the cis-1,4-polymerization catalyst. In another method, the first polymerization mixture can be prepared by mixing the controlled 1,3-butadiene solution with the aluminum catalytic ingredient (a') consisting of at least one organic aluminum compound of the formula (Ia):



wherein R and X are the same as defined above, by aging the resultant mixture for at least one minute and then by admixing the aged admixture with the cobalt catalytic ingredient (b).

In the above-mentioned first polymerization mixture-preparation method including the aging procedure, it is important that the mixture of the controlled 1,3-butadiene solution with the aluminum catalytic ingredient be aged for one minute or more in the absence of the cobalt catalytic ingredient. This aging procedure is effective for enhancing the catalytic activity of the resultant cis-1,4-polymerization catalyst, for restricting formation of a gel in the first polymerization step, and for restricting deposit of polymer (including the gel) onto

the inside surface of a vessel in which the cis-1,4-polymerization is carried out. The above-mentioned effects of the aging procedure are also effective for prolonging the lifetime in which the vessel can be continuously used for not only the cis-1,4-polymerization but also the 1,2-polymerization.

The above-mentioned effects of the aging procedure can be further enhanced by preventing contamination of water into the aged mixture after the aging procedure is completed.

If a mixture of the inert organic solvent and the aluminum catalytic ingredient (a') is aged in the absence of 1,3-butadiene or if a mixture of the controlled 1,3-butadiene solution with the cobalt catalytic ingredient (b) is aged, the above-mentioned effects of the aging procedure are extremely small. It is thus impossible to prevent the deposit of the cis-1,4-polybutadiene onto the cis-1,4-polymerization vessel.

The aging procedure of the mixture consisting of the controlled 1,3-butadiene solution and the aluminum catalytic ingredient (a) is carried out for at least one minute, preferably, from 2 minutes to 2 hours, preferably, at a temperature of 10° C. to 80° C., more preferably, 10° C. to 50° C. If the aging time is less than one minute, it is difficult to attain the above-mentioned effects of the aging procedure.

After the aging procedure is completed, the aged mixture is preferably cooled to a temperature of 10° C. or less. The resultant cooled mixture is then admixed with the cobalt catalytic ingredient (b) while the admixture is stirred.

It is preferable that the cis-1,4-polymerization catalyst contain the aluminum catalytic ingredient (a) or (a') in an amount of at least 0.1 millimole, more preferably, from 0.5 to 50 millimoles, per mole of 1,3-butadiene in the first polymerization mixture. Also, it is preferable that it contain the cobalt catalytic ingredient (b) in an amount of at least 0.001 millimole, more preferably, at least 0.005 millimole, still more preferably, from 0.007 to 0.07 millimoles, per mole of 1,3-butadiene in the first polymerization mixture. Furthermore, it is preferred that the cis-1,4-polymerization catalyst have a molar ratio of the aluminum catalytic ingredient (a) or (a') to the cobalt catalytic ingredient (b) of at least 5:1, more preferably, at least 15:1, still more preferably, from 50:1 to 500:1.

The resultant first polymerization mixture is subjected to the cis-1,4-polymerization at a temperature of, preferably, from -20° C. to 80° C., more preferably, from 5° C. to 50° C., for a polymerization time, i.e., the average time for which the first polymerization mixture resides in the cis-1,4-polymerization vessel, of from 10 minutes to 10 hours, while the mixture is stirred in the vessel. The polymerization vessel for the cis-1,4-polymerization is not limited to a specific type of vessel. For example, a polymerization vessel with a high viscosity stirring apparatus, for instance, as disclosed in Japanese Examined Patent Publication (Kokoku) No. 40-2645, can be used for carrying out the cis-1,4-polymerization procedure.

In the cis-1,4-polymerization procedure, it is preferred that the resultant polybutadiene contain 90% or more, more preferably, 95% or more, of cis-1,4-structure and exhibit an intrinsic viscosity of 1.5 to 8.0, more preferably, 1.5 to 5.0, determined in toluene at a temperature of 30° C.

In order to produce the cis-1,4-polybutadiene having a desired intrinsic viscosity  $[\eta]$  toluene 30° C., the mo-

lecular weight of the resultant cis-1,4-polybutadiene can be controlled by adding a molecular weight modifier to the first polymerization mixture. The molecular weight modifier preferably consists essentially of at least one member selected from non-conjugated diene compounds, for example, cyclooctadiene and allen $\pi$  (isoallylene), ethylene, and  $\alpha$ -olefin compounds, for instance, propylene and butene-1.

In order to prevent the formation of a gel in the cis-1,4-polymerization, it is preferred that an anti-gelling agent be added to the first polymerization mixture. The anti-gelling agent may be selected from conventional anti-gelling agents.

After the cis-1,4-polymerization procedure is completed, a second polymerization mixture containing the resultant cis-1,4-polybutadiene in step (B) and non-reacted 1,3-butadiene, which are dissolved in the inert organic solvent, and a 1,2-polymerization catalyst is subjected to a 1,2-polymerization. The second polymerization mixture can be prepared by mixing the resultant cis-1,4-polymerization mixture obtained in step (B) with the 1,2-polymerization catalyst and, if necessary, an additional amount of fresh 1,3-butadiene which has been preferably cooled to a temperature of 10° C. or less. In this case, it is preferred that the amount of the non-reacted 1,3-butadiene in the second polymerization mixture be in the range of from 3% to 35% by weight.

The 1,2-polymerization catalyst comprises a cobalt catalytic ingredient (c) consisting of at least one cobalt compound, an aluminum catalytic ingredient (d) consisting of at least one organic aluminum compound of the formula (II):



(II)

wherein R is the same as defined above, and another catalytic ingredient (e) consisting of carbon disulfide.

The cobalt compounds usable for the cobalt catalytic ingredient (c) can be selected from the same group of cobalt compounds as those usable for the cobalt catalytic ingredient (b).

The aluminum compounds of the formula (II) are preferably selected from the group consisting of triethyl aluminum, trimethyl aluminum, triisobutyl aluminum, and triphenyl aluminum.

The carbon disulfide is preferably free from water.

Each of the catalytic ingredients may be fed, in the form of a solution thereof in the inert organic solvent or in 1,3-butadiene, to the second polymerization mixture. The solution is preferably cooled to a temperature of 10° C. or less.

In the second polymerization mixture, the amount of the 1,2-polymerization catalyst is variable depending on the types of the catalytic ingredients, component of the catalyst, and the polymerization conditions. However, it is preferred that the cobalt catalytic ingredient (c) be used in an amount of 0.005 millimole or more, preferably, from 0.01 to 5 millimoles; the aluminum catalytic ingredient (d) in an amount of at least 0.1 millimole, preferably, from 0.5 to 50 millimoles; and carbon disulfide (e) in an amount of at least 0.001 millimole, more preferably, from 0.01 to 10 millimoles, each per mole of 1,3-butadiene in the second polymerization mixture.

In the case where the type of the cobalt catalytic ingredient (b) in the cis-1,4-polymerization catalyst is the same as that of the cobalt catalytic ingredient (c) in the 1,2-polymerization catalyst, the cis-1,4-polymerization catalyst may contain the cobalt compound in an

amount necessary for both the first and second polymerization procedures. In this case, the second polymerization mixture can be prepared by mixing the resultant first polymerization mixture which contains the cobalt catalytic ingredient, in the necessary amount for the 1,2-polymerization catalyst, with the aluminum catalytic ingredient and carbon disulfide.

The second polymerization mixture is subjected to the 1,2-polymerization procedure preferably at a temperature of from  $-20^{\circ}\text{C}$ . to  $80^{\circ}\text{C}$ ., more preferably, from  $5^{\circ}\text{C}$ . to  $50^{\circ}\text{C}$ . for 10 minutes to 10 hours, under either atmospheric pressure or increased pressure.

The 1,2-polymerization procedure is carried out by stirring the second polymerization mixture in a polymerization vessel. Since the second polymerization mixture exhibits a high viscosity during the 1,2-polymerization procedure, the resultant polymer tends to deposit onto the surface of the polymerization vessel. Therefore, it is preferable that the polymerization vessel be provided with a device for removing the deposited polymer, as described in Japanese Examined Patent Publication No. 40-2645.

After the 1,2-polymerization procedure is completed, it is preferred that the resultant 1,2-polymerization mixture which contains the resultant polybutadiene rubber, non-reacted 1,3-butadiene, carbon disulfide, cobalt catalytic ingredient(s), aluminum catalytic ingredients, and inert organic solvent be moved to a polymerization shortstopping vessel and that a polymerization shortstopper be added to the 1,2-polymerization mixture so as to shortstop the 1,2-polymerization.

The polymerization shortstopper is not limited to a specific type of compounds as long as the compounds can be reacted with the aluminum compounds of the formula (II) so as to deactivate the aluminum catalytic ingredient (d). Usually, the polymerization shortstopper consists of at least one member selected from aliphatic alcohols, for example, methyl alcohol and ethyl alcohol; water; inorganic acids, for example, hydrochloric acid and sulfuric acid; organic acids, for instance, acetic acid and benzoic acid; monoethanolamine; ammonia; phosphorous esters, for example, tris(nonylphenyl)phosphite; and hydrogen chloride gas. The polymerization shortstopper may be in the form of an aqueous solution or an alcoholic solution.

After the 1,2-polymerization procedure is terminated, the resultant 1,2-polymerization mixture is subjected to a step for isolating the resultant polybutadiene rubber therefrom. This isolation can be effected by adding a precipitating agent, for example, methyl alcohol to the polymerization mixture or by evaporating volatile substances from the polymerization mixture while blowing or not blowing steam into the polymerization mixture, so as to cause the polybutadiene rubber to deposit from the polymerization mixture. The deposited polybutadiene rubber is separated from the polymerization mixture, washed with methyl alcohol or hot water, and then dried.

In order to protect the polybutadiene rubber from degradation, it is preferred that an anti-oxidant be added to the resultant polymerization mixture during the shortstopping procedure, or be added to a slurry of the polybutadiene rubber.

In the 1,2-polymerization procedure, a polybutadiene rubber consisting essentially of 5% to 30%, preferably, 7% to 15% by weight of a boiling n-hexane-insoluble fraction and 70% to 95%, preferably, 85% to 93%, by weight of a boiling n-hexane-soluble fraction thereof, is

obtained. The boiling n-hexane-insoluble fraction usually exhibits a melting point of from  $180^{\circ}\text{C}$ . to  $215^{\circ}\text{C}$ .

After the polybutadiene rubber is isolated from the polymerization mixture, the isolation residue is subjected to a recovery procedure in which the non-reacted 1,3-butadiene and the inert organic solvent, which are substantially free from carbon disulfide, are recovered.

In the recovery procedure, the non-reacted 1,3-butadiene and the inert organic solvent are recovered by means of distillation. The carbon disulfide is eliminated by means of adsorption thereof on an adsorbing agent or of addition reaction thereof with a reactant capable of reacting with carbon disulfide and of forming an addition reaction product insoluble in the inert organic solvent, soluble in water, or having a boiling point significantly higher than that of 1,3-butadiene and the inert organic solvent.

In a recovery method, first, a mixture of the non-reacted 1,3-butadiene, the inert organic solvent, and carbon disulfide is distilled from the isolation residue of the 1,2-polymerization mixture. Then, the carbon disulfide is removed from the distilled mixture by means of the adsorption of the addition reaction.

In another recovery method, carbon disulfide is eliminated from the isolation residue of the 1,2-polymerization mixture by means of the adsorption or the addition reaction so as to provide a remaining solution free from carbon disulfide. Then, the non-reacted 1,3-butadiene and the inert organic solvent are recovered from the remaining solution by means of distillation.

In still another recovery method, first, a mixture of the non-reacted 1,3-butadiene and carbon disulfide is distilled from the residue of the second polymerization mixture so as to provide a distillation residue containing the inert organic solvent and being substantially free from carbon disulfide; second, the carbon disulfide is eliminated from the distilled mixture by means of the adsorption or the addition reaction so as to provide the non-reacted 1,3-butadiene substantially free from carbon disulfide; and, finally, the inert organic solvent is recovered from the distillation residue by means of distillation.

In the adsorption elimination, carbon disulfide is adsorbed by an adsorbing agent consisting of, for example, a basic anion exchange resin which usually contains amino radicals. This adsorption elimination can be carried out either in a batch-type procedure or in a flow-type continuous procedure at a temperature of from  $5^{\circ}\text{C}$ . to  $60^{\circ}\text{C}$ . for a contact time of from one to 60 minutes. The basic anion exchange resin can be selected from commercial basic anion exchange resins, for instance, Amberlite IR-45 (trademark, made by Rohm & Haas), Diaion WA-21 (trademark, made by Mitsubishi Chemical Ind.), Dowex 3 (trademark, made by Dow Chemical), and Dulite A-7 (trademark, made by Diamond Shamrock). When the adsorption elimination is carried out in the batch-type procedure, it is preferable that the basic anion exchange resin be used in an amount of from 0.1 to 10 parts by volume per 100 parts by volume of the liquid containing the carbon disulfide. When the flow-type continuous procedure is applied to the adsorption elimination, it is preferable that the carbon disulfide-containing liquid be passed at a space velocity of from 2 to 15 through the adsorbing agent. The term "space velocity" refers to the quotient of the flow rate of the liquid in  $\text{m}^3/\text{hr}$  with the volume of the



adsorbing agent in  $m^3$  and is usually expressed by an absolute number.

In the adsorption elimination of carbon disulfide, it is preferable that the basic anion exchange resin be swollen with an inert organic solvent before the resin is brought into contact with the carbon disulfide-containing liquid.

The adsorption of carbon disulfide by a weak basic anion exchange resin causes a small amount of hydrogen sulfide ( $H_2S$ ) to be generated by a side reaction. Therefore, it is preferable that the adsorption residue liquid be washed with water or be treated with a strong basic anion exchange resin, for example, Diaion PA-316 (trademark, made by Mitsubishi Chemical Ind.), to eliminate the  $H_2S$  from the residual liquid.

The resultant carbon disulfide-adsorbed anion exchange resin can be reactivated by washing it with an acid aqueous solution and then with an alkali aqueous solution. The adsorbed carbon disulfide is recovered by the above-mentioned washing operation. The recovered carbon disulfide is refined and then is recycled to step (D).

In the addition reaction elimination of carbon disulfide, a carbon disulfide-containing liquid is brought into contact with a reactant which is capable of producing an addition reaction product with carbon disulfide. The resultant addition reaction product must be insoluble in the inert organic solvent, be soluble in water, or have a boiling point higher than that of 1,3-butadiene and the inert organic solvent. The reactant usually consists of at least one nitrogen-containing compound, for example, selected from the group consisting of aliphatic amine compounds, for example, melamine, guanidine, ethylene diamine, 1,6-hexamethylenediamine, 1,12-dodecamethylenediamine, diethylenetriamine, diethylamine, n-octylamine, n-lauroamine, and di-n-butylamine; aromatic amine compounds, for example, aniline, 2,4-diaminophenol, 2,4-diaminotoluene, 2,6-diaminotoluene, 2,2'-diaminodiphenylmethane, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 3,5-diaminobenzoic acid, p-diaminoazobenzene, 4,4'-disaminodiphenylamine, benzidine, 3,3'-diaminobenzidine, 1,2,4,5-tetraminobenzene, p,p'-diaminodiphenyl oxide, piperidine, and benzylamine; and cycloaliphatic amine compounds, for example, cyclohexylamine and cyclopentylamine.

The nitrogen-containing reactant is added to a carbon disulfide-containing liquid. The amount of the reactant is preferably in the range of from 1 to 20 moles per mole of carbon disulfide contained in the liquid. The mixture of the reactant with the carbon disulfide-containing liquid is stirred at a temperature of from  $5^\circ C.$  to  $60^\circ C.$  for from 5 to 120 minutes so as to promote the reaction between the reactant with carbon disulfide. The resultant addition product is separated from the mixture by washing the mixture with water, distilling the mixture, filtering the mixture, or centrifuging the mixture.

After the recovery procedure is completed, the resultant mixture of 1,3-butadiene and the inert organic solvent, which mixture is substantially free from carbon disulfide, can be recycled to step (A). In this case, if necessary, necessary amounts of fresh 1,3-butadiene and inert organic solvent are added to the recycled mixture to provide a desired amount of the 1,3-polybutadiene solution having a desired concentration of 1,3-butadiene.

The process of the present invention will be further explained by referring to the accompanying drawings.

In FIG. 1, fresh 1,3-butadiene contained in a tank 1 is introduced into a mixer 3 through a conduit 20 and a recovered solution of 1,3-butadiene in an inert organic solvent having a higher boiling point than that of 1,3-butadiene, for example, benzene, from a tank 2 into the mixer 3 through a conduit 21. The fresh 1,3-butadiene and the recovered 1,3-butadiene solution are mixed with each other in the mixer 3 to provide a 1,3-butadiene solution having a desired concentration of 1,3-butadiene. The 1,3-butadiene solution is introduced from the mixer 3 into a mixer 4 through a conduit 22. In order to control the concentration of water in the 1,3-butadiene solution to a desired value, water is fed into the conduit 22 through a water-supply conduit 23. The 1,3-butadiene solution is uniformly mixed with water in the mixer 4. The resultant controlled 1,3-butadiene solution is supplied into a cis-1,4-polymerization vessel 5 through a conduit 24. An aluminum catalytic ingredient and a cobalt catalytic ingredient are fed into the vessel 5 through a conduit 25 and a conduit 28, respectively. Also, a molecular weight modifier consisting of, for example, cyclooctadiene and an anti-gelling agent consisting of, for example, dilauryl-3,3'-thiodipropionate are fed into the vessel 5 through a conduit 26 and a conduit 27, respectively. The resultant first polymerization mixture is stirred in the vessel 5 to produce a cis-1,4-polybutadiene. The resultant polymerization mixture containing cis-1,4-polybutadiene is transferred from the vessel 5 to a 1,2-polymerization vessel 6 through a conduit 29. A cobalt catalytic ingredient is supplied to the vessel 6 through a conduit 30, an aluminum catalytic ingredient consisting of the aluminum compound of the formula (II) is fed into the vessel 6 through a conduit 31, and carbon disulfide is fed into the vessel 6 through a conduit 32. The aluminum catalytic ingredient and/or carbon disulfide may be fed into the conduit 29. The resultant second polymerization mixture in the vessel 6 is stirred so as to allow the cis-1,4-polybutadiene and the non-reacted 1,3-butadiene to be converted to a polybutadiene rubber consisting essentially of 5% to 30% by weight of a boiling n-hexane-insoluble fraction and 70% to 95% by weight of a boiling n-hexane-soluble fraction. During the 1,2-polymerization procedure, a polymer insoluble in the inert organic solvent deposits from the polymerization mixture onto the inside surface of the vessel 6 and the viscosity of the polymerization increases. Therefore, it is preferable that the 1,2-polymerization vessel 6 have an agitator equipped with a device for removing the deposited polymer from the inside surface of the vessel.

The resultant polymerization mixture in the 1,2-polymerization vessel 6 is introduced into a polymerization shortstopping vessel 40 through a conduit 33. Also, a polymerization shortstopper is fed into the vessel 40 through a conduit 34 so as to shortstop the 1,2-polymerization. The polymerization shortstopped mixture is introduced into an isolating apparatus 7 through a conduit 35. In the isolating apparatus 7, the resultant polybutadiene rubber is isolated so as to leave an isolation residue containing non-reacted 1,3-butadiene, the inert organic solvent, and carbon disulfide. The isolated polybutadiene rubber is removed through a passage 8. The isolation residue is introduced into an apparatus 9 for eliminating carbon disulfide from the isolation residue by means of adsorption or addition reaction. The

eliminated carbon disulfide is removed from the apparatus 9 through a passage 10.

The residue containing the non-reacted 1,3-butadiene and the inert organic solvent and retained in the apparatus 9 is fed into a distillation apparatus 11 which may be composed of a single distillation column or of two or more distillation columns, through a conduit 37. In the distillation apparatus, a mixture of the non-reacted 1,3-butadiene and the inert organic solvent, which mixture is substantially free from carbon disulfide, is recovered and introduced into the tank 2 through a conduit 38. A distillation residue containing a high boiling point substance is removed from the distillation apparatus 11 through a passage 12. Referring to FIG. 2, the apparatus is composed of the same devices as those indicated in FIG. 1, with the following exceptions. That is, an aging vessel 13 is inserted between the mixer 4 and the cis-1,4-polymerization vessel 5. The mixer 4 is connected to the aging vessel 13 through the conduit 24 and a conduit 25 for feeding an aluminum catalytic ingredient of the cis-1,4-polymerization catalyst is connected to the conduit 24. The aging vessel 13 is connected to the cis-1,4-polymerization vessel 5 through a conduit 39.

The controlled 1,3-butadiene solution is mixed with the aluminum catalytic ingredient in the conduit 24 and the resultant mixture is aged in the aging vessel 13 for a predetermined time period. The aged mixture is fed into the cis-1,4-polymerization vessel 5 through the conduit 39 and is mixed in the vessel 5 with a molecular weight modifier fed through the conduit 26, an anti-gelling agent fed through the conduit 27, and a cobalt catalytic ingredient fed through the conduit 28.

The above-mentioned aging procedure is effective for reducing the amount of the cobalt catalytic ingredient necessary for obtaining the cis-1,4-polymerization catalyst having a satisfactory catalytic activity. Accordingly, the resultant polybutadiene rubber contains a reduced amount of residual cobalt. This feature is effective for reducing the degradation of the polybutadiene rubber products.

#### SPECIFIC EXAMPLES

The present invention will be further explained in the following examples. In the examples, the amount of the boiling n-hexane-insoluble fraction of the resultant polybutadiene rubber was determined by immersing 2 g of the polybutadiene rubber in 200 ml of n-hexane at room temperature, by separating a fraction of the rubber insoluble in n-hexane by means of filtration, by extracting the n-hexane insoluble fraction at a boiling point of n-hexane by using a Soxhlet's extractor for 4 hours, by separating the non-extracted fraction from n-hexane, by drying it under vacuum, and, finally, measuring the weight of the dried fraction.

The amount of the boiling n-hexane-soluble fraction of the polybutadiene rubber was determined by subjecting the resultant extracted solution from the above-mentioned extraction procedure to an evaporation procedure in which n-hexane was evaporated from the solution, drying the residual fraction under vacuum, then measuring the weight of the dried fraction.

The content of the cis-1,4-structure in the boiling n-hexane-soluble fraction in the polybutadiene rubber and the content of the cis-1,4-structure in the cis-1,4-polymerization product were determined by means of infrared absorption spectrum analysis (IR).

The content of the 1,2-structure in the boiling n-hexane-insoluble fraction of the polybutadiene rubber was

determined by means of nuclear magnetic resonance spectrum (NMR).

The melting point of the boiling n-hexane-insoluble fraction of the polybutadiene rubber was determined from a temperature at a peak point appearing in an endothermic curve of the polybutadiene rubber measured by a recording differential scanning calorimeter (DSC).

The intrinsic viscosities  $[\eta]$  of the boiling n-hexane-soluble fraction of the polybutadiene rubber and of the cis-1,4-polymerization product were determined in toluene at a temperature of 30° C.

The reduced viscosity  $[\eta_{sp}/c]$  of the boiling n-hexane-insoluble fraction of the polybutadiene rubber was determined in tetrahydronaphthalene at a temperature of 135° C.

The concentration of carbon disulfide in a carbon disulfide-containing liquid was determined by using a gas chromatograph equipped with a flame spectrophotometer and containing therein a filler consisting of chromosolve 102 (trademark, made by Gasukuro Kogyo Co., Ltd.).

#### Example 1

A solution containing 23.7% by weight of 1,3-butadiene dissolved in benzene was dehydrated by using a dehydrating column. The dehydrated 1,3-butadiene solution was mixed with 40 mg/l (2.2 millimoles/l) of water and the mixture was stirred so as to allow water to be dissolved in the 1,3-butadiene solution. The resultant controlled solution was cooled to a temperature of -3° C., the was continuously introduced at a flow rate of 50 l/hr into a cis-1,4-polymerization vessel. The vessel was a stainless steel autoclave having an inside volume of 20 liters and equipped with double helical-type stirring paddles and a jacket for controlling the temperature of the contents of the autoclave. An aqueous solution of calcium chloride ( $\text{CaCl}_2$ ) was circulated through the jacket at a temperature of -10° C.

Also, into the cis-1,4-polymerization vessel, diethylaluminum monochloride was introduced at a flow rate of 25.3 g/hr, 1,5-cyclooctadiene at a flow rate of 60.0 g/hr, dilauryl-3,3'-thiodipropionate (TPL) at a flow rate of 7.0 g/hr, and cobalt octoate at a flow rate of 260 mg/hr. The resultant first polymerization mixture was stirred at a temperature of 40° C. for an average residing time of 24 minutes to cis-1,4-polymerize the 1,3-butadiene. During the cis-1,4-polymerization procedure, cis-1,4-polybutadiene was produced at a rate of 3.22 kg/hr. The resultant polymer contained 96% or more of cis-1,4-structure and had an intrinsic viscosity of 1.8. The content of gel produced in the polymer was 0.02% by weight, determined by using a 200 mesh screen. The resultant polymerization mixture in the cis-1,4-polymerization vessel was introduced at a flow rate of 50 liters/hr into a 1,2-polymerization vessel of the same type as the cis-1,4-polymerization vessel. Also, the 1,2-polymerization vessel was fed with triethylaluminum at a flow rate of 27.3 g/hr, cobalt octoate at a flow rate of 842 mg/hr, and carbon disulfide at a flow rate of 840 mg/hr. The resultant second polymerization mixture was stirred at a temperature of 40° C. for an average residing time of 24 minutes so as to 1,2-polymerize the non-reacted 1,3-butadiene. The resultant polymerization mixture was continuously introduced into a polymerization shortstopping vessel equipped with stirring paddles and was mixed with a small amount of tris (non-ylphenol) phosphite and then with water so as to short-

stop the 1,2-polymerization reaction. The resultant mixture was introduced at a flow rate of 120 liters/hr into a steam stripper equipped with stirring paddles and was mixed with hot water and saturated steam introduced into the stripper under a pressure of 4 kg/cm<sup>2</sup> G. The mixture was dispersed in the hot water so as to allow the volatile substances in the mixture to evaporate away. The resultant aqueous slurry of the polybutadiene was removed from the steam stripper. The polybutadiene rubber in the form of crumbs and water were separated from the aqueous slurry. The separated polybutadiene rubber was dried at room temperature under vacuum.

The above-mentioned procedures were continuously carried out for 14 hours. The polybutadiene rubber was produced at a rate of 3.62 kg/hr. The polybutadiene rubber contained 11.1% of a boiling n-hexane-insoluble fraction having a melting point of 205° C. and a reduced viscosity [ $\eta_{sp}/C$ ] of 2.1 (dl/g) and containing 93.1% of 1,2-structure. The remaining boiling n-hexane soluble fraction of the polybutadiene rubber contained 96.9% of cis-1,4-structure and had an intrinsic viscosity of 1.8.

After the polymerization procedures were completed, a fresh 1,3-butadiene solution was passed through the polymerization apparatus at a flow rate of 50 liters/hr for 30 minutes. Thereafter, the polymer adhering on the inside surface of the polymerization vessels and on the surfaces of the stirring paddles was collected. The collected polymer was dried under vacuum. The amount of the polymer collected in the cis-1,4-polymerization vessel was 18 g containing 3 g of gel. The amount of the polymer collected in the 1,2-polymerization vessel was 99 g.

The volatile substance evaporated from the steam stripper was cooled and was condensed. The condensed substance was separated into an aqueous phase and an organic solvent phase. The organic solvent phase was isolated from the aqueous phase. A portion of the isolated organic solvent solution was subjected to an elimination process of carbon disulfide, and to a recovery process of 1,3-butadiene, and benzene in the following manner.

The isolated organic solvent solution, which contained 16.1% by weight of 1,3-butadiene and 12.5 mg/l of carbon disulfide and was in an amount of 300 liters, was passed at a flow rate of 50 liters/hr at a temperature of 15° C. to 20° C. through a first adsorption column. The first column contained therein an adsorption filler having a height of 70 cm and a diameter of 10 cm and consisting of a basic anion exchange resin available under a trademark of Diaion WA-20, made by Mitsubishi Chemical Ind. It was then passed through a second absorption column. The second column contained therein an absorption filler which had a height of 30 cm and diameter of 10 cm and consisted of a strong basic anion exchange resin available under a trademark of Diaion PA-316, made by Mitsubishi Chemical Ind. This eliminated the carbon disulfide from the organic solvent solution. The organic solvent solution discharged from the second adsorption column was substantially free from carbon disulfide and was distilled at a temperature of 120° C. to 160° C. so as to leave a high boiling point substance. The distilled solution consisted of 1,3-butadiene and benzene and recycled to the water-controlling step.

The anion exchange resins used were reactivated by treating them with an aqueous HCl solution and then with an aqueous NaOH solution.

By the above-mentioned adsorption procedures, 98% or more of the carbon disulfide was eliminated from the isolated organic solvent solution. The resultant solution of 1,3-butadiene in benzene was substantially free from carbon disulfide.

The remaining portion of the isolated organic solvent solution was subjected to another elimination process of carbon disulfide, and to the same recovery process of 1,3-butadiene and benzene as that described above.

That is, 300 liters of the isolated organic solvent solution was mixed with 65 g of hexamethylenediamine. The mixture was stirred at a room temperature of about 20° C. for 50 minutes. Next, 90 liters of a 1% sodium hydroxide aqueous solution was added to the mixture. The admixture was vigorously stirred and, thereafter, was left standing so as to allow an aqueous phase to be separated from an organic solvent solution phase. After the aqueous phase was removed, the remaining organic solvent solution was mixed with 90 liters of water, was stirred, and was left standing to remove an aqueous phase from an organic solvent solution phase. The above-mentioned procedures were repeated twice. The resultant organic solvent solution was washed with water and distilled to remove a high boiling point substance therefrom.

By the above-mentioned procedures, 95% or more of carbon disulfide was removed from the organic solvent solution. The resultant solution of 1,3-butadiene in benzene was substantially free from carbon disulfide. The recovered 1,3-butadiene solution was recycled to the water-controlling step.

#### Example 2

The same procedures as those described in Example 1 were carried out with the following exceptions.

The same controlled 1,3-butadiene solution as that described in Example 1 was introduced at a flow rate of 50 liters/hr into an aging vessel equipped with stirring paddles and having an inside volume of 20 liters while diethylaluminum monochloride was introduced at a flow rate of 25.0 g (208 millimoles)/hr into the aging vessel. The resultant mixture was aged in the aging vessel at a temperature of 30° C. for an average residence time of 24 minutes. The aged mixture was cooled to a temperature of -3° C. and then introduced at a flow rate of 50 liters/hr into the same type of cis-1,4-polymerization vessel as that described in Example 1, while introducing, into the cis-1,4-polymerization vessel, cobalt octoate at a flow rate of 264 mg (0.77 millimoles)/hr, 1,5-cyclooctadiene at a flow rate of 60.0 g (0.556 moles)/hr, and dilauryl-3,3'-thiodipropionate (TPL) at a flow rate of 7.0 g (13.6 millimoles)/hr, to provide the first polymerization mixture.

By the cis-1,4-polymerization procedure at a polymerization temperature of 40° C. for an average residing time of 24 minutes, cis-1,4-polybutadiene was produced at a rate of 3.52 kg/hr. The resultant polymer contained 98% or more of cis-1,4-structure and had an intrinsic viscosity of 1.9 and on content of gel of 0.01% or less which was determined by using a 200 mesh screen.

The resultant polymerization mixture was introduced at a flow rate of 50 liters/hr into the same type of 1,2-polymerization vessel as that described in Example 1, while introducing, into the 1,2-polymerization vessel, triethylaluminum at a flow rate of 27.5 g (241 millimoles)/hr, cobalt octoate at a flow rate of 840 mg (2.36 millimoles)/hr, and carbon disulfide at a flow rate of 750 mg (9.87 millimoles)/hr. The resultant second poly-

merization mixture was subjected to the 1,2-polymerization under the same conditions as those described in Example 1.

The 1,2-polymerization reaction was shortstopped by introducing the polymerization mixture into the same type of polymerization shortstopping vessel as that described in Example 1 and by mixing it with 2,6-di-tert-butyl-4-methylphenol in an amount of 1 part per 100 parts of the resultant polybutadiene rubber and with a small amount of methyl alcohol.

The procedures for producing the polybutadiene rubber were continuously carried out for 16 hours. The polybutadiene rubber was obtained in an amount of 4,00 kg/hr and contained 12.0% by weight of the boiling n-hexane-insoluble fraction thereof. The boiling n-hexane-insoluble fraction exhibited a melting point of 205° C. and a reduced viscosity [ $\eta_{sp}/C$ ] of 2.1 (dl/g) and contained 93.1% of 1,2-structure. The remaining boiling n-hexane-soluble fraction of the resultant polybutadiene rubber contained 96.9% of cis-1,4-structure and had an intrinsic viscosity [ $\eta$ ] of 1.8.

After the cis-1,4-polymerization vessel and the 1,2-polymerization vessel were washed with the fresh 1,3-butadiene solution in the same manner as that described in Example 1, it was found that the polymer removed from the cis-1,4-polymerization vessel was in an amount of 12 g including 2 g of gel and the polymer removed from the 1,2-polymerization vessel was in an amount of 98 g.

The non-reacted 1,3-butadiene, the inert organic solvent (benzene), and carbon disulfide were recovered by the following manner.

The organic solvent solution was isolated from the residue of the resultant polymerization mixture in the same manner as that described in Example 1. The isolated solution contained 15.6% by weight of 1,3-butadiene and 12 mg/l of carbon disulfide.

Three hundred liters of the isolated organic solvent solution was passed at a flow rate of 50 liters/hr at a temperature of 15° C. to 20° C. through a first absorption column containing therein an absorption filler having a height of 70 cm and a diameter of 10 cm and consisting of a basic anion exchange resin (Amberlite IR-45, containing 5.5 meq/g of amino radicals), and then through the same second adsorption column as that described in Example 1, to eliminate carbon disulfide from the organic solvent solution. The adsorption procedure resulted in elimination of carbon disulfide in an amount of 98% or more from the isolated organic solvent solution. The organic solvent solution discharged from the second adsorption column was a solution of 1,3-butadiene in benzene and was free from carbon disulfide.

#### Examples 3 and 4

In Example 3, the polybutadiene rubber produced in Example 1 was converted into a composition as indicated in Table 1.

TABLE 1

Component	Amount (part by weight)
Polybutadiene rubber	100
HAF Carbon Black(*)	50
Aromatic process oil	10
Zinc oxide	5
Stearic acid	2
Amine type antioxidant	1
Cyclohexyl-benzothiazyl sulfenamide	1

TABLE 1-continued

Component	Amount (part by weight)
Sulfur	1.5

Note:

Oil adsorption: 120 g per 100 g of the carbon black  
Surface area: 85 m<sup>2</sup> per g of the carbon black

The composition was uniformly mixed by using a Bambury mixer having a capacity of 1.7 l and, then, by using a roll mill, and vulcanized at a temperature of 140° C. for 30 minutes. The vulcanizing procedure was applied to a portion of the composition which was subjected to the measurement of a cut growth resistance of the vulcanized rubber, at 140° C. for 75 minutes. The properties of the vulcanized rubber was determined in accordance with Japanese Industrial Standard K-6301.

In Example 4, the same procedures as those described in Example 3 were carried out except that the polybutadiene rubber used was one produced in Example 2.

For the purpose of comparison, the same procedures as those mentioned above were carried out, except that the polybutadiene rubber was replaced by a commercially available high cis-1,4-polybutadiene.

The properties of the vulcanized rubber of the present example and the comparative vulcanized rubber are indicated in Table 2.

TABLE 2

Item	Ex-ample 3	Ex-ample 4	Comparative Composition
Hardness	71	71	60
300% modulus (kg/cm <sup>2</sup> )	147	145	83
Ultimate elongation (%)	400	400	540
Tensile strength (kg/cm <sup>2</sup> )	183	181	190
Tear resistance (kg/cm <sup>2</sup> )(*) <sub>1</sub>	59	61	48
Resilience %	50	50	64
Cut growth resistance(*) <sub>2</sub>	65,000	71,000	3,000

Note:

(\*)<sub>1</sub>The tear resistance was measured by using B-type dumbbell described in JIS K-6301.

(\*)<sub>2</sub>The cut growth resistance was measured by the De Mattia flexmachine and was represented by the number of flexing operations at which the length of a crack in a testing specimen reached from 2 mm to 15 mm.

We claim:

1. A process for producing a polybutadiene rubber with enhanced mechanical strength, comprising the successive steps of:

(A) mixing 1,3-butadiene with an inert organic solvent to provide a 1,3-butadiene solution;

(B) controlling a concentration of water contained in said 1,3-butadiene solution to from 0.2 to 5 millimoles per liter of said 1,3-butadiene solution;

(C) subjecting a first polymerization mixture which comprises said controlled 1,3-butadiene solution and a cis-1,4-polymerization catalyst comprising:

(a) an aluminum catalytic ingredient consisting of at least one organic aluminum compound of the formula (I):



(I)

wherein R represents a member selected from the group consisting of alkyl radicals having 1 to 6 carbon atoms, a phenyl radical and cycloalkyl radicals, X represents a halogen atom and n represents the number of 1.5 to 2.0, and

(b) a cobalt catalytic ingredient consisting of at least one cobalt compound soluble in said inert organic solvent,

- to a cis-1,4-polymerization to convert at least a portion of said 1,3-butadiene contained in said first polymerization mixture to cis-1,4-polybutadiene;
- (D) subjecting a second polymerization mixture which comprises the resultant cis-1,4-polybutadiene, non-reacted 1,3-butadiene, the organic solvent, and an 1,2-polymerization catalyst comprising:
- (c) a cobalt catalytic ingredient consisting of at least one cobalt compound soluble in the inert organic solvent,
- (d) an aluminum catalytic ingredient consisting of at least one organic aluminum compound of the formula (II):



(II)

wherein R is the same as defined above, and

- (e) carbon disulfide, to a 1,2-polymerization to provide a polybutadiene rubber consisting essentially of 5% to 30% by weight of a boiling n-hexane-insoluble fraction and 95 to 70% of a n-hexane-soluble fraction;
- (E) stopping said 1,2-polymerization by adding a polymerization shortstopper to the resultant second polymerization mixture; and
- (F) isolating the resultant polybutadiene rubber from the stopped second polymerization mixture.
2. The process as claimed in claim 1, wherein the amount of 1,3-butadiene in said 1,3-butadiene solution in step (A) is at least 3% based on the sum of the weights of 1,3-butadiene and said inert organic solvent.
3. The process as claimed in claim 1, wherein said inert organic solvent consists essentially of at least one member selected from the group consisting of aromatic hydrocarbons, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, and halogenated derivatives of the above-mentioned hydrocarbons.
4. The process as claimed in claim 1, wherein in step (B), the amount of water in said 1,3-butadiene solution is controlled to a range of from 0.5 to 5 millimoles per liter of said 1,3-butadiene solution.
5. The process as claimed in claim 1, wherein said first polymerization mixture is prepared by mixing the controlled 1,3-butadiene solution with said cis-1,4-polymerization catalyst.
6. The process as claimed in claim 1, wherein said controlled 1,3-butadiene solution is cooled to a temperature of 10° C. or less.
7. The process as claimed in claim 1, wherein said aluminum compound of the formula (I) in said cis-1,4-polymerization catalyst is selected from the group consisting of diethyl aluminum monochloride, diethyl aluminum monobromide, diisobutyl aluminum monochloride, and ethyl aluminum sesquichloride.
8. The process as claimed in claim 1, wherein said cobalt compound in said cis-1,4-polymerization catalyst is selected from the group consisting of cobalt  $\beta$ -ketone complexes, cobalt  $\beta$ -ketoacid ester complexes, cobalt salts of organic carboxylic acids having 6 or more carbon atoms, cobalt halide complexes and cobalt complexes coordinated with butadiene.
9. The process as claimed in claim 1, wherein the amount of said aluminum catalyst ingredient (a) in said cis-1,4-polymerization catalyst is at least 0.1 millimole per mole of 1,3-butadiene in said first polymerization mixture.

10. The process as claimed in claim 1, wherein the amount of said cobalt catalytic ingredient (b) in said cis-1,4-polymerization catalyst is at least 0.001 millimole per mole of 1,3-butadiene in said first polymerization mixture.

11. The process as claimed in claim 1, wherein the molar ratio of said aluminum catalytic ingredient (a) to said cobalt ingredient (b) in said cis-1,4-polymerization catalyst is at least 5.0.

12. The process as claimed in claim 1, wherein said first polymerization mixture is prepared by mixing the controlled 1,3-butadiene solution of step (B) with an aluminum catalytic ingredient (a') consisting of at least one organic aluminum compound of the formula (Ia):



(Ia)

wherein R and X are the same as defined above, by aging the resultant mixture for at least one minute, and, then, by admixing said aged mixture with said cobalt catalytic ingredient (b).

13. The process as claimed in claim 12, wherein said aging operation is carried out at a temperature of from 10° C. to 80° C.

14. The process as claimed in claim 12, wherein said organic aluminum compound of the formula (Ia) is selected from the group consisting of diethyl aluminum monochloride, diethyl aluminum monobromide, and diisobutyl aluminum monochloride.

15. The process as claimed in claim 1, wherein said cis-1,4-polymerization is carried out at a temperature of from -20° C. to 80° C.

16. The process as claimed in claim 1, wherein the resultant cis-1,4-polybutadiene in step (C) contains at least 90% of cis-1,4-structure and has an intrinsic viscosity of from 1.5 to 8 determined in toluene at a temperature of 30° C.

17. The process as claimed in claim 1, wherein said first polymerization mixture further contains a molecular weight modifier and/or an anti-gelling agent.

18. The process as claimed in claim 1, wherein said aluminum compound of the formula (II) in said 1,2-polymerization catalyst is selected from the group consisting of triethyl aluminum, trimethyl aluminum, triisobutyl aluminum, and triphenyl aluminum.

19. The process as claimed in claim 1, wherein said cobalt compound in said 1,2-polymerization catalyst is selected from the group consisting of cobalt  $\beta$ -ketone complexes, cobalt  $\beta$ -ketoacid ester complexes, cobalt salts of organic carboxylic acids having 6 or more carbon atoms, cobalt halide complexes and cobalt complexes coordinated with butadiene.

20. The process as claimed in claim 1, wherein said aluminum catalytic ingredient (d) in said 1,2-polymerization catalyst is in an amount of at least 0.1 millimole per mole of said non-reacted 1,3-butadiene in said second polymerization mixture.

21. The process as claimed in claim 1, wherein said cobalt catalytic ingredient (c) in said 1,2-polymerization catalyst is in an amount of at least 0.005 millimole per mole of said non-reacted 1,3-butadiene in said second polymerization mixture.

22. The process as claimed in claim 1, wherein said carbon disulfide in said 1,2-polymerization catalyst is in an amount of at least 0.001 millimole per mole of said non-reacted 1,3-butadiene in said second polymerization mixture.

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23. The process as claimed in claim 1, wherein said 1,2-polymerization is carried out at a temperature of from  $-20^{\circ}\text{C.}$  to  $80^{\circ}\text{C.}$

24. The process as claimed in claim 1, wherein said second polymerization mixture contains said non-reacted 1,3-butadiene in a concentration of from 3% to 35% by weight.

25. The process as claimed in claim 1, wherein said polymerization shortstopper consists of at least one member selected from the group consisting of aliphatic alcohols, water, inorganic acids, organic acids, monoethanolamine, ammonia, phosphorous esters and hydrogen chloride.

26. The process as claimed in claim 24, wherein said shotstopper is in the form of a solution thereof dissolved in water and/or aliphatic liquid alcohols.

27. The process as claimed in claim 1, wherein the isolation of said polybutadiene rubber from the resultant 1,2-polymerization mixture is carried out by adding a precipitation agent to said resultant second polymerization mixture in step (F).

28. The process as claimed in claim 1, wherein the isolation of said polybutadiene rubber is carried out by evaporating volatile substances from the resultant 1,2-polymerization mixture.

29. The process as claimed in claim 1, wherein after said polybutadiene rubber is isolated from said 1,2-

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polymerization mixture, the isolation residue is subjected to a recovery procedure of a mixture of non-reacted 1,3-butadiene and said inert organic solvent, which mixture is substantially free from carbon disulfide.

30. The process as claimed in claim 29, wherein said mixture of non-reacted 1,3-butadiene and the inert organic solvent is recycled to said step (A).

31. The process as claimed in claim 29, wherein carbon disulfide is eliminated from said isolation residue.

32. The process as claimed in claim 31, wherein said carbon disulfide is eliminated by means of adsorption thereof on an adsorbing agent or of addition reaction thereof with a reactant capable of reacting with carbon disulfide and of forming an addition reaction product insoluble in said inert organic solvent, soluble in water, or having a boiling point significantly higher than that of 1,3-butadiene and said inert organic solvent.

33. The process as claimed in claim 32, wherein said adsorbing agent consists of a basic anion exchange resin containing amino radicals.

34. The process as claimed in claim 32, wherein said reactant consists of at least one nitrogen-containing compound selected from the group consisting of aliphatic amine compounds, aromatic amino compound, and cycloaliphatic amine compounds.

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## ⑫ 特 許 公 報 (B 2)

昭63-36324

⑬ Int. Cl.<sup>4</sup>C 08 F 295/00  
4/60  
6/10

識別記号

MRK

庁内整理番号

6681-4J

⑭公告 昭和63年(1988)7月20日

発明の数 1 (全9頁)

⑮発明の名称 補強ポリブタジエンゴムの製造方法

⑯特 願 昭56-208108

⑰公 開 昭58-109513

⑱出 願 昭56(1981)12月24日

⑲昭58(1983)6月29日

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## ㉖特許請求の範囲

1 1, 3-ブタジエンをシス-1, 4重合し、  
ついで1, 2-重合する方法において、

(a) 1, 3-ブタジエンと不活性有機溶媒とを混  
合し、

(b) 得られた1, 3-ブタジエンの不活性有機溶  
媒溶液中の水分の濃度を調節し、

(c) 得られた溶液にシス-1, 4重合触媒の一成分  
である一般式 $\text{AlR}_2\text{X}$ (ただし、Rは炭素数1  
~6のアルキル基、フェニル基またはシクロア  
ルキル基であり、Xはハロゲン原子である。)   
で表わされるハロゲン含有の有機アルミニウム  
化合物を添加し、得られた混合液をコバルト化  
合物の不存在下に1分間以上熟成した後、

(d) シス-1, 4重合触媒の他の一成分であるコ   
バルト化合物を添加し、得られた溶液を攪拌混  
合し1, 3-ブタジエンを重合してシス-1,   
4ポリブタジエンを生成させ、

(e) 得られた重合反応混合液中に、コバルト化合  
物と一般式  $\text{AlR}_2$

(ただし、Rは前記と同じである。) で表わ

される有機アルミニウム化合物と、二硫化炭素  
とから得られる1, 2重合触媒を存在させて、  
1, 3-ブタジエンを重合し、沸騰n-ヘキサン  
不溶分5~30重量%と沸騰n-ヘキサン可溶分  
95~70重量%とからなる最終ポリブタジエンゴ  
ムを生成させ、

(f) 得られた重合反応混合物に重合停止剤を添加  
した後、固形分であるポリブタジエンゴムを分  
離取得し、

10 (g) 残部の未反応の1, 3-ブタジエン、不活性  
有機溶媒および二硫化炭素を含有する混合物か  
ら、蒸留によつて1, 3-ブタジエンと不活性  
有機溶媒とを留分として取得するとともに、二  
硫化炭素を分離除去し、二硫化炭素を実質的に  
含有しない1, 3-ブタジエンと不活性有機溶  
媒とを前記の(a)工程に循環させる、

ことを特徴とする補強ポリブタジエンゴムの製造  
方法。

## 発明の詳細な説明

20 この発明は、沸騰n-ヘキサン不溶分5~30重  
量%と沸騰n-ヘキサン可溶分95~70重量%とか

らなる補強ポリブタジエンゴムの製造方法に関するものである。

1, 3-ブタジエンをシス-1, 4重合触媒の存在下に重合して得られるシス-1, 4構造含有率の高いシス-1, 4ポリブタジエンは、タイヤその他のゴム製品の原料として大量に製造、販売されている。シス-1, 4ポリブタジエンから得られたゴム製品の物理的性質が、特に反発弾性の良いこと、発熱量の小さいこと、耐摩耗性の優れていることなどの点で天然ゴムからのゴム製品よりも優れていることが、シス-1, 4ポリブタジエンの大量に使用されている理由の一つである。しかしながら、シス-1, 4ポリブタジエンは、これから得られたゴム製品の引裂強度が小さく、耐屈曲亀裂成長特性が小さいという欠点を有している。

このシス-1, 4ポリブタジエンの有する欠点を改良したポリブタジエンゴムとして、1, 3-ブタジエンをシス-1, 4重合触媒の存在下に重合してシス-1, 4ポリブタジエンを生成させ、続いて1, 2重合触媒の存在下に1, 3-ブタジエンを重合することによつて得られる新規なポリブタジエンが提案された(特公昭49-17666号)。

上記公報には、加硫すると引裂強度が大きく耐屈曲亀裂成長性が優れたポリブタジエンの製造実験例が記載されている。

しかし、上記公報に記載されているポリブタジエンの製造法は、1, 2重合触媒の一成分として二硫化炭素を用い、この二硫化炭素を1, 2重合槽に添加する方法であり、二硫化炭素は重合反応終了後1, 3-ブタジエンや不活性有機溶媒と、特に1, 3-ブタジエンと、蒸留によつては完全に分離することが困難であり、二硫化炭素の取扱いがむづかしく、そのため前記ポリブタジエンの製造を実用化することが困難であつた。

そこで、この発明者らは、上記の優れた物性を有するポリブタジエンゴムの連続的な製造方法を提供することを目的として鋭意研究した結果、蒸留と二硫化炭素の吸着分離処理あるいは二硫化炭素付加物分離処理などの処理とを組み合わせ、二硫化炭素と1, 3-ブタジエンおよび不活性有機溶媒とを分離することによつて、この目的が達成されることを見出し、この発明を完成した。

すなわち、この発明は、1, 3-ブタジエンを

シス-1, 4重合し、ついでシンジオー1, 2重合する方法において、

(a) 1, 3-ブタジエンと不活性有機溶媒とを混合し、

(b) 得られた1, 3-ブタジエンの不活性有機溶媒溶液中の水分の濃度を調節し、

(c) 得られた溶液に、シス-1, 4重合触媒の一成分である一般式 $\text{AIRX}_2$ (ただし、Rは炭素数1~6のアルキル基、フェニル基またはシクロアルキル基であり、Xはハロゲン原子である。)で表わされるハロゲン含有の有機アルミニウム化合物を添加し、得られた混合液をコバルト化合物の不存在下に1分間以上熟成した後、

(d) シス-1, 4重合触媒の他の一成分であるコバルト化合物を添加し、得られた溶液を攪拌混合し1, 3-ブタジエンを重合してシス-1, 4ポリブタジエンを生成させ、

(e) 得られた重合反応混合液中に、コバルト化合物と一般式 $\text{AIR}_3$ (ただし、Rは前記と同じである。)で表わされる有機アルミニウム化合物と、二硫化炭素とから得られる1, 2重合触媒を存在させて、1, 3-ブタジエンを重合し、沸騰n-ヘキサン不溶分5~30重量%と沸騰n-ヘキサン可溶分95~70重量%とからなる最終ポリブタジエンゴムを生成させ、

(f) 得られた重合反応混合物に重合停止剤を添加した後、固形分であるポリブタジエンゴムを分離取得し、

(g) 残部の未反応の1, 3-ブタジエン、不活性有機溶媒および二硫化炭素を含有する混合物から、蒸留によつて1, 3-ブタジエンと不活性有機溶媒とを留分として取得するとともに、二硫化炭素を分離除去し、二硫化炭素を実質的に含有しない1, 3-ブタジエンと不活性有機溶媒とを前記の(a)工程に循環させる、

ことを特徴とする補強ポリブタジエンゴムの製造方法に関するものである。

この発明の方法においては、最初の(a)工程において、1, 3-ブタジエンと不活性有機溶媒とを、好ましくは1, 3-ブタジエンと不活性有機溶媒とに合計量に対する1, 3-ブタジエンの割合が3重量%以上、特に3~40重量%の範囲となるように混合する。

ついで(b)工程において、前述のようにして得ら



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れた1, 3-ブタジエンの不活性有機溶媒溶液中の水分の濃度を調節する。この発明の方法において、溶液中に既に所定量の水が存在する場合には、次の(c)工程に移ることができる。水分は、前記の溶液1ℓ中に0.5〜5ミリモルの濃度で含有されることが好ましい。水分の濃度を調節するにはそれ自体公知の方法が採用できる。

この発明の方法においては、溶液中の水分の濃度を調節した後、(c)工程において、得られた溶液にシスー1, 4重合触媒の一成分である一般式  $AlR_2X$  で表わされるハロゲン含有の有機アルミニウム化合物を添加し、得られた混合液をコバルト化合物の不存在下に1分間以上熟成する。この発明において、前記の方法によつてハロゲン含有の有機アルミニウム化合物を添加した混合液を、コバルト化合物の不存在下に熟成することが必要であり、これによつて、シスー1, 4重合触媒の活性が向上し、シス重合時のゲルの生成を抑制することができ、シス重合槽内へのポリマー（ゲルを含む）の付着を抑制することができ、このためシス重合だけでなく、1, 2重合も含めた全体の連続重合時間をのばすことができる。前記の熟成効果は、熟成後の溶液中に水分を入れないようにすると顕著である。1, 3-ブタジエンを含有しない混合液を熟成しても、あるいはハロゲン含有の有機アルミニウム化合物のかわりにコバルト化合物を添加した混合液を熟成しても熟成の効果は小さく、シス重合槽内へのポリマーの付着を抑制することはできない。

ハロゲン含有の有機アルミニウム化合物を添加した混合液を熟成する時間は、1分間以上、好ましくは2分〜2時間であり、熟成する温度は10〜80℃、特に10〜50℃が好ましい。熟成する時間が1分間より少ないと、熟成の効果が小さくなる。

前記の不活性有機溶媒としては、形成されるシスー1, 4ポリブタジエンを溶解しうる有機溶媒であれば特に制限はないが、ベンゼン、トルエン、キシレンなどの芳香族炭化水素、n-ヘプタン、n-ヘキサンなどの脂肪族炭化水素、シクロヘキサン、メチルシクロヘキサンなどの脂環族炭化水素などの炭化水素溶媒、およびそれらのハロゲン化物、例えば塩化メチレン、クロルベンゼンなどが挙げられ、特に炭化水素溶媒が好適に使用できる。

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シスー1, 4重合触媒のアルミニウム成分である前記の一般式  $AlR_2X$  で表わされるハロゲン含有の有機アルミニウム化合物としては、ジエチルアルミニウムモノクロライド、ジエチルアルミニウムモノブロマイド、ジイソブチルアルミニウムモノクロライドなどを挙げることができる。前記のハロゲン含有の有機アルミニウム化合物の使用量は、1, 3-ブタジエン1モルに対して0.1ミリモル以上、特に0.5〜50ミリモルが好ましい。

1, 3-ブタジエンおよび水分を含有する不活性有機溶媒溶液にハロゲン含有の有機アルミニウム化合物を添加した混合液を熟成した後、好ましくは得られた熟成溶液を10℃以下に冷却した後、(d)工程において、シスー1, 4重合触媒の他の一成分であるコバルト化合物を添加し、得られた溶液を攪拌混合し1, 3-ブタジエンを重合してシスー1, 4ポリブタジエンを生成させる。

シスー1, 4重合触媒の一成分であるコバルト化合物は、使用する不活性有機溶媒に可溶なものであればどのようなものでもよい。例えば、このようなコバルト化合物としては、コバルト(II)アセチルアセトナート、コバルト(III)アセチルアセトナートなどのコバルトのβ-ジケトン錯体、コバルトアセト酢酸エチルエステル錯体のようなコバルトのβ-ケト酸エステル錯体、コバルトオクトエート、コバルトナフテネート、コバルトベンゾエートなどの炭素数6以上の有機カルボン酸のコバルト塩、塩化コバルトピリジン錯体、塩化コバルトエチルアルコール錯体などのハロゲン化コバルト錯体などを挙げることができる。

コバルト化合物の使用量は、1, 3-ブタジエン1モルに対して0.001ミリモル以上、特に0.005ミリモル以上であることが好ましい。

また、コバルト化合物に対するハロゲン含有の有機アルミニウム化合物のモル比(Al/Co)は5以上、特に15以上であることが好ましい。

この発明の方法においてシス重合の重合温度は、-20〜80℃、特に5〜50℃が好ましく、重合圧力は常圧または加圧のいずれでもよく、重合時間（重合槽内での平均滞留時間）は10分〜10時間の範囲が好ましい。また、シス重合はシス重合反応槽にて溶液を攪拌混合して行なう。シス重合に用いる重合反応槽としては、高粘度液攪拌装置付きの重合反応槽、例えば、特公昭40-2645号公報

に記載されている装置を用いることができる。

前記のシス重合は、シス-1, 4構造含有率90%以上、特に95%以上で、トルエン30°Cの固有粘度 $[\eta]$ <sub>トルエン</sub><sup>30°C</sup>1.5~8、特に1.5~5であるシス-1, 4ポリブタジエンが生成するように行なうのが好ましい。 $[\eta]$ <sub>トルエン</sub><sup>30°C</sup>を適当な値とするために、公知の分子量調節剤、例えば、シクロオクタジエン、アレンなどの非共役ジエン類、またはエチレン、プロピレン、ブテン-1などの $\alpha$ -オレフィンを使用することができる。また、シス重合時のゲルの生成をさらに抑えるために公知のゲル防止剤を使用することもできる。

この発明の方法においては、(e)工程において、前記の(d)工程：シス重合工程で得られた重合反応混合液中に、コバルト化合物と一般式AIR<sub>3</sub>で表わされる有機アルミニウム化合物と、二硫化炭素とから得られる1, 2重合触媒を存在させて、1, 3-ブタジエンを重合し、沸騰n-ヘキサン不溶分5~30重量%と沸騰n-ヘキサン可溶分95~70重量%とからなる最終ポリブタジエンゴムを生成させる。

1, 2重合触媒のアルミニウム成分である前記の一般式AIR<sub>3</sub>で表わされる有機アルミニウム化合物としては、トリエチルアルミニウム、トリメチルアルミニウム、トリイソブチルアルミニウム、トリフェニルアルミニウムなどを挙げることができる。

1, 2重合触媒の一成分である二硫化炭素は特に限定されないが水分を含まないものであることが好ましい。

1, 2重合触媒のコバルト成分としては、前記のシス重合触媒の一成分であるコバルト化合物として挙げられたものと同じものが挙げられる。

1, 2重合触媒の使用量は、触媒各成分の種類および組合せ、並びに重合条件によつて相違するが、1, 3-ブタジエン1モル当り、コバルト化合物が0.005ミリモル以上、特に0.01~5ミリモル、有機アルミニウム化合物が0.1ミリモル以上、特に0.5~50ミリモル、二硫化炭素が0.001ミリモル以上、特に0.01~10ミリモルであることが好ましい。

この発明の方法において、シス重合触媒のコバルト化合物と1, 2重合触媒のコバルト化合物とが同一である場合には、シス重合時に、1, 2重

合にも必要な量のコバルト化合物を合わせて添加し、1, 2重合時には有機アルミニウム化合物と二硫化炭素とを添加するだけにする条件を選ぶこともできる。

この発明の方法において1, 2重合の重合温度は、-20~80°C、特に5~50°Cが好ましく、重合圧力は常圧または加圧のいずれでもよく、重合時間は10分~10時間の範囲が好ましい。また、1, 2重合は1, 2重合槽にて、溶液を攪拌混合して行なう。1, 2重合に用いる重合槽としては、1, 2重合中に重合反応混合物がさらに高粘度となり、ポリマーが重合槽内に付着しやすいので、特公昭40-2645号公報に記載されているような掻取り部材を備えた重合槽を用いることが好ましい。

1, 2重合の際、重合系における1, 3-ブタジエンの濃度は3~35重量%であることが好ましい。

この発明の方法においては、(f)工程において、前記の(e)工程：1, 2重合工程で得られたポリブタジエンゴム、未反応の1, 3-ブタジエン、二硫化炭素、コバルト化合物、有機アルミニウム化合物および不活性有機溶媒を含有する重合反応混合物を、好ましくは重合停止槽に供給し、この重合反応混合物に、重合停止剤を添加して重合を停止した後、固形分であるポリブタジエンゴムを分離取得する。

前記の重合停止剤としては、前述の一般式AIR<sub>3</sub>Xで表わされるハロゲン含有の有機アルミニウム化合物および一般式AIR<sub>3</sub>で表わされる有機アルミニウム化合物と反応する化合物であればよく、例えば、メタノール、エタノールなどのアルコール、水、塩酸、硫酸などの無機酸、酢酸、安息香酸などの有機酸、モノエタノールアミンやアンモニア、あるいは塩化水素ガスなどが挙げられる。これらは、単味で重合反応混合物に添加してもよく、水、アルコールに混合して添加してもよい。

1, 3-ブタジエンの重合を停止した後、重合反応混合物にメタノールなどの沈殿剤を加えるか、あるいはフラツシュ（水蒸気を吹きこむかあるいは吹きこまずして揮発分を蒸発除去する。）し固形分である重合体を析出させ、分離乾燥してポリブタジエンゴムを得ることができる。このポ

リブタジエンゴムには、1, 3-ブタジエンの重合を停止した後の重合反応混合物あるいはポリブタジエンゴムのスラリーなどに老化防止剤を添加する方法などによつて、老化防止剤を配合することが好ましい。

この発明の方法によつて得られるポリブタジエンゴムは、沸騰 *n*-ヘキサン不溶分が5~30重量%であり、沸騰 *n*-ヘキサン可溶分95~70重量%であり、沸騰 *n*-ヘキサン不溶分の融点が180~215°Cである。

この発明の方法においては、(g) 工程において、重合反応混合物から固形分であるポリブタジエンゴムを分離取得した残部の、未反応の1, 3-ブタジエン、不活性有機溶媒および二硫化炭素を含有する混合物（通常回収溶剤といわれる）から、蒸留によつて1, 3-ブタジエンと不活性有機溶媒とを留分として取得し、一方二硫化炭素の吸着分離処理あるいは二硫化炭素付加物分離処理などの処理によつて、二硫化炭素を分離除去し、二硫化炭素を実質的に含有しない1, 3-ブタジエンと不活性有機溶媒とを回収する。

前記の3成分を含有する混合物から、アミノ基含有イオン交換樹脂のような塩基性陰イオン交換樹脂を用いる吸着分離処理によつて二硫化炭素を分離除去するか、あるいは、二硫化炭素と反応して、不活性有機溶媒に不溶な付加物、水溶性の付加物、あるいは1, 3-ブタジエンおよび不活性有機溶媒よりも明らかに高い沸点を有する付加物を形成する窒素含有化合物を二硫化炭素と反応させ、生成した付加物を溶液からそれ自体公知の方法で分離する二硫化炭素付加物分離処理によつて二硫化炭素を分離除去した後、蒸留によつて、二硫化炭素を実質的に含有しない1, 3-ブタジエンと不活性有機溶媒とを留分として回収することができる。

また、前記の3成分を含有する混合物から、蒸留によつて、前記の3成分を留分として回収し、この留分から、前述の吸着分離あるいは二硫化炭素付加物分離処理によつて二硫化炭素を分離除去することによつても、二硫化炭素を実質的に含有しない1, 3-ブタジエンと不活性有機溶媒とを回収することができる。

または、前記の3成分を含有する混合物から、蒸留によつて、二硫化炭素を含有する1, 3-ブ

タジエンを留分として、二硫化炭素を実質的に含有しない不活性有機溶媒を釜残として取得し、前記の留分から、前述の吸着分離あるいは二硫化炭素付加物分離処理によつて二硫化炭素を分離除去し、一方、前記の釜残から蒸留によつて不活性有機溶媒を留分として取得することによつても、二硫化炭素を実質的に含有しない1, 3-ブタジエンと不活性有機溶媒とを回収することができる。

前記の塩基性陰イオン交換樹脂を用いる二硫化炭素の吸着分離処理は、バッチ法で行なつてもよく、あるいは流通法で行なつてもよく、5~60°Cで1~60分間（滞留時間）行なうことが好ましい。前記の塩基性陰イオン交換樹脂としては、一般に市販されているアンバーライトIR-45、ダイヤイオンWA-21、ダウエックス3、デューライトA-7などの弱塩基性陰イオン交換樹脂を用いることができる。バッチ法で処理する場合には、塩基性陰イオン交換樹脂の量は処理する溶液100容量部当り0.1~10容量部が好ましい。また、流通法で処理する場合には、空間速度（Space Velocity）〔1時間当りの通流量( $m^3/hr$ )を充填剤の体積( $m^3$ )で除した値で通常単位を付さないで示される〕は2~15が好ましい。塩基性陰イオン交換樹脂は処理前に不活性有機溶媒で膨潤させるのが好ましい。また、弱塩基性陰イオン交換樹脂を用いて二硫化炭素を除去する際に、微量の $H_2S$ が副生するので、弱塩基性陰イオン交換樹脂で処理した液をさらに水洗するか、あるいはダイヤイオンPA-316のような強塩基性陰イオン交換樹脂を用いて $H_2S$ を除くのが好ましい。

また、前記の二硫化炭素付加物分離処理は、処理する溶液中に、該溶液中に含有される二硫化炭素1モルに対して1~20モルの窒素含有化合物を添加し、5~60°Cで5~120分間攪拌混合して二硫化炭素と窒素含有化合物とを反応させた後、反応生成物を溶液から分離して行なうことが好ましい。前記の反応生成物を含む溶液を水洗、蒸留、滷過あるいは遠心分離などして、溶液から二硫化炭素と窒素含有化合物との反応生成物を分離すればよい。前記の窒素含有化合物としては、メラミン、グアニジン、エチレンジアミン、1, 6-ヘキサメチレンジアミン、1, 12-ドデカメチレンジアミン、ジエチレントリアミン、ジエチルアミン、*n*-オクチルアミン、*n*-ラウロアミン、ジ

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—*n*—ブチルアミンなどの脂肪族アミン：アニリン、2, 4—ジアミノフェノール、2, 4—ジアミノトルエン、2, 6—ジアミノトルエン、2, 2′—ジアミノジフェニルメタン、2, 4′—ジアミノジフェニルメタン、4, 4′—ジアミノジフェニルメタン、*o*—フェニレンジアミン、*m*—フェニレンジアミン、*p*—フェニレンジアミン、3, 5—ジアミノ安息香酸、*p*—ジアミノアゾベンゼン、4, 4′—ジアミノジフェニルアミン、ベンジジン、3, 3′—ジアミノベンジジン、1, 2, 4, 5—テトラアミノベンゼン、*p,p'*—ジアミノジフェニルオキサイド、ピペリジン、ベンジルアミンなどの芳香族アミン、シクロヘキシルアミン、シクロペンチルアミンなどの脂環族アミンなどが挙げられる。

前記した方法により回収された二硫化炭素を実質的に含有しない1, 3—ブタジエンと不活性有機溶媒は、前記の(a)工程に循環することができる。

上記のようにして循環された二硫化炭素を実質的に含有しない1, 3—ブタジエンと不活性有機溶媒とは、補充の新しい1, 3—ブタジエンと混合して使用される。

また、二硫化炭素を吸着した塩基性陰イオン交換樹脂は酸洗浄、ついでアルカリ洗浄によつて二硫化炭素の回収と塩基性陰イオン交換樹脂の再生をすることができ、回収した二硫化炭素は精製した後、前記の(e)工程に循環することができる。

以下、この発明の方法を実施するさいに不活性有機溶媒としてベンゼンのような1, 3—ブタジエンの沸点より高い沸点を有する不活性有機溶媒を用いた一態様を示す第1図のフローシートを用いて、この発明をさらに説明する。ただし、この発明の範囲は以下の記載に限定されるものではない。

第1図において、フレッシュ1, 3—ブタジエンタンク1から導管20により送入された1, 3—ブタジエンと、精製された回収溶剤タンク2から導管21により送入された精製された回収溶剤(1, 3—ブタジエンと不活性有機溶媒との混合物)とが混合機3にて混合される。得られた1, 3—ブタジエンのベンゼン溶液は導管22を経て混合機4に導かれる。1, 3—ブタジエンのベンゼン溶液には、導管23から適当量の水が供給さ

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れる。混合機4において、1, 3—ブタジエンのベンゼン溶液と水とは均一に混合された後、導管24を経て熟成槽5に導かれる。水分の濃度を調節した1, 3—ブタジエンのベンゼン溶液には、導管25からハロゲン含有の有機アルミニウムが供給される。熟成槽5では、ハロゲン含有の有機アルミニウム化合物を添加した混合液が、コバルト化合物の不存在下に1分間以上熟成される。熟成槽5にて熟成された混合液は、導管26を経てシスー1, 4重合反応槽6に供給される。また、前記シスー1, 4重合反応槽6には、導管27からシクロオクタジエンのような分子量調節剤が、導管28からTPLのようなゲル防止剤が、導管29からコバルト化合物がそれぞれ供給される。シスー1, 4重合反応槽6では、溶液を攪拌混合してシスー1, 4ポリブタジエンを生成させる。

シスー1, 4重合反応槽6で得られた重合反応混合液は、導管30を経て1, 2重合反応槽7に供給される。また、前記1, 2重合反応槽7には、導管31からコバルト化合物が、導管32から一般式 $\text{AlR}_3$ で表わされる有機アルミニウム化合物が、導管33から二硫化炭素がそれぞれ供給される(図面には示していないが、一般式 $\text{AlR}_3$ で表わされる有機アルミニウム化合物およびあるいは二硫化炭素は導管30中に供給してもよい)。これらコバルト化合物と一般式 $\text{AlR}_3$ で表わされる有機アルミニウム化合物と二硫化炭素とから得られる1, 2重合触媒の存在下に、混合物を攪拌して1, 3—ブタジエンを重合し、沸騰*n*—ヘキサン不溶分5~30重量%と沸騰*n*—ヘキサン可溶分95~70重量%とからなる最終ポリブタジエンゴムを生成させる。1, 2重合反応槽7中で1, 3—ブタジエンを重合するさいに、不活性有機溶媒に不溶なポリマーが析出してき、かつ重合反応混合物が高粘度となるため、1, 2重合反応槽としては掻取り部材を備えた攪拌機付きの重合反応槽が好適に使用される。

1, 2重合反応槽7で得られた重合反応混合物は、導管34を経て重合停止槽40に供給される。一方、前記の重合反応混合物には重合停止槽40において導管35から重合停止剤を供給して1, 3—ブタジエンの重合を停止する。重合を停止された混合物は導管36を経て補強ポリブタジエンゴム分離装置8に供給され、重合反応混合物

から、固形分である補強ポリブタジエンゴム 9 と、未反応の 1, 3-ブタジエン、不活性有機溶媒および二硫化炭素を含有する液体の混合物とが分離される。

補強ポリブタジエンゴム分離装置 8 によつて固形分である補強ポリブタジエンゴムを分離した残部の前記の液体の混合物は、導管 37 を経て二硫化炭素の吸着分離処理あるいは二硫化炭素付加物分離処理の処理器 10 に供給される。前記の処理器 10 によつて、前記の液体の混合物から、二硫化炭素 11 が分離除去される。

二硫化炭素の吸着分離処理あるいは二硫化炭素付加物分離処理などの処理器 10 によつて二硫化炭素を除去された 1, 3-ブタジエンおよび不活性有機溶媒を含有する液体の混合物は、導管 38 を経て蒸留装置 12 (1つの蒸留塔でもよく、2つの蒸留塔でもよい) に供給される。蒸留装置 12 によつて、二硫化炭素を実質的に含有しない 1, 3-ブタジエンと不活性有機溶媒とが分離され、これらは導管 39 を経て、精製された回収溶剤タンク 2 に供給される。また、蒸留装置 12 から高沸点物 13 が分離除去される。

この発明の方法によると、コバルト化合物の使用量が少なくなるため補強ポリブタジエンゴムに含まれる灰分量が減少し、最終ゴム製品にしたときに優れた物性を示す補強ポリブタジエンゴムを連続的に製造することができる。

次に実施例を示す。実施例の記載において、補強ポリブタジエンゴムの沸騰  $n$ -ヘキサン不溶分は、2g の補強ポリブタジエンゴムを 200ml の  $n$ -ヘキサンに室温で大部分を溶解させた後、不溶分を 4 時間ソクスレー抽出器によつて抽出し、抽出残分を真空乾燥し、その重量を精秤して求めたものである。また、沸騰  $n$ -ヘキサン可溶分は、上記のようにして得られた  $n$ -ヘキサン溶解分およびソクスレー抽出器による抽出分から  $n$ -ヘキサンを蒸発除去した後、真空乾燥し、その重量を精秤して求めたものである。また、補強ポリブタジエンゴムの  $n$ -ヘキサン可溶分およびシスー 1, 4 重合後のポリブタジエンのシスー 1, 4 構造含有率は赤外吸収スペクトル (IR) により測定し、 $n$ -ヘキサン不溶分の 1, 2-構造含有率は核磁気共鳴スペクトル (NMR) により測定し、 $n$ -ヘキサン不溶分の融点は自記差動熱量計

(DSC) による吸熱曲線のピーク温度により決定した。

また、補強ポリブタジエンゴムの  $n$ -ヘキサン可溶分およびシスー 1, 4 重合後のポリブタジエンの極限粘度  $[\eta]$  については 30°C、トルエン中で測定した値であり、補強ポリブタジエンゴムの  $n$ -ヘキサン不溶分の還元粘度  $\eta_{sp}/C$  については、135°C、テトラリン中で測定した値である。

また、溶液中の二硫化炭素の含有量は、株式会社日立製作所の炎光光度検出器を持つガスクロマトグラフィーを使用し、充填剤としてクロモソルブ 102 を用いて測定し、算出した。

#### 実施例

1, 3-ブタジエンを 23.7 重量% 含有する 1, 3-ブタジエンのベンゼン溶液から脱水塔により水分を除き、得られた溶液に水を 40mg (2.2 ミリモル) /  $\ell$  の割合で添加後、攪拌翼付の混合槽で混合し溶解させた。この溶液を内容積 20  $\ell$  の攪拌翼付熟成槽に毎時 50  $\ell$  の割合で供給し、ジエチルアルミニウムモノクロライドを毎時 25.0 g (208 ミリモル) 混入し、混合液を 30°C で 24 分間 (平均滞留時間) 熟成した。得られた熟成液を、-3°C に冷却後、内容積 20  $\ell$  のリボン型攪拌翼付のステンレス製オートクレーブで外筒に温度調節用のジャケットを備え、-10°C の  $\text{CaCl}_2$  水溶液を該ジャケットに循環させたシスー 1, 4 重合槽に毎時 50  $\ell$  の割合で供給し、コバルトオクトエートを毎時 264mg (0.77 ミリモル)、1, 5-シクロオクタジエンを毎時 60.0 g (0.556 モル)、TPL (ジラウリルー 3, 3'-チオジプロピオネート) を毎時 7.0 g (13.6 ミリモル) 供給し、重合温度 40°C、平均滞留時間 24 分間にてシスー 1, 4 重合した。このシスー 1, 4 重合による 1 時間当りのポリブタジエン生成量は 35.2kg であり、このポリブタジエンは、シスー 1, 4 構造含有率が 98% 以上であり、 $[\eta]$  が 1.9 であり、200 メツシュの金網を用いて測定したゲル分が 0.01% 以下であった。

シスー 1, 4 重合槽で得られた重合反応混合液を、シスー 1, 4 重合槽と同じ型の重合槽 (1, 2 重合槽) に毎時 50  $\ell$  の割合で連続的に供給し、トリエチルアルミニウムを毎時 27.5 g (241 ミリモル)、コバルトオクトエートを毎時 840mg (2.36 ミリモル)、二硫化炭素を毎時 750mg (9.87 ミリモル) 供給し、重合温度 40°C、平均滞留時間 24 分間

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にて1, 2重合した。得られた重合反応混合物を攪拌翼付混合槽に連続的に供給し、これに2, 6-ジ第3ブチル-4-メチルフェノールをゴムに対して1PHR加え、さらに少量のメタノールを混入して重合を停止した。この混合物を、攪拌翼付の溶剤蒸発槽（スチームストリッパー）に毎時120ℓで供給し、熱水および4 kg/cm<sup>2</sup>Gの飽和水蒸気を供給し、混合物を熱水中に分散させ、溶剤を蒸発させた。

蒸発槽からスラリーを抜き出し、水と分散ポリブタジエンの屑（クラム）とを分離した後、クラムを常温で真空乾燥して補強ポリブタジエンゴムを得た。

16時間連続的に重合して、重合時間1時間当たり平均4.00kgの補強ポリブタジエンゴムが得られた。この補強ポリブタジエンゴムは、沸騰n-ヘキサン不溶分が12.0%であり、沸騰n-ヘキサン不溶分は融点が205℃であり、 $\eta_{sp}/C$ が2.1(dℓ/g)であり、1, 2-構造含有率が93.1%であり、沸騰n-ヘキサン可溶分はシス-1, 4構造含有率が96.9%であり、 $[\eta]$ が1.8であつた。

重合反応終了後、1, 3-ブタジエンのベンゼン溶液を毎時50ℓの割合で30分間流した後、重合槽内の攪拌翼および内壁に付着しているポリマーをかき落とし、真空乾燥して付着ポリマーを得た。付着ポリマー量は、シス-1, 4重合槽では12g（うちゲル分が2g）であり、1, 2重合槽では98gであつた。

一方、蒸発槽から蒸発した溶剤は冷却凝縮して水相と溶剤相とに分離後、得られた溶剤（回収溶剤という）から、以下のようにして1, 3-ブタ

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ジエンとベンゼンとを回収した。

1, 3-ブタジエンを15.6重量%、二硫化炭素を12mg/ℓの割合でそれぞれ含有する回収溶剤700ℓを、塩基性陰イオン交換樹脂（アンバーライトIR-45：アミノ基5.5meq/g）を充填した充填塔（充填高さ70cm、充填塔内径10cm）について強塩基性の陰イオン交換樹脂（ダイヤイオンPA-316）を充填した充填塔（充填高さ30cm、充填塔内径10cm）に15~20℃で毎時50ℓの割合で流通させて二硫化炭素を除去した後、蒸留によつて高沸点物を除き、重合溶剤とし、重合溶剤を再使用した。陰イオン交換樹脂の再生は、通常のHCl洗浄およびNaOH洗浄により行なつた。前記処理により、回収溶剤中の二硫化炭素は98%以上が除去され、二硫化炭素を実質的に含有しない1, 3-ブタジエンとベンゼンとを回収された。

#### 図面の簡単な説明

第1図は、この発明の方法を実施するさいに不活性有機溶媒としてベンゼンのような1, 3-ブタジエンの沸点よりも高い沸点を有する不活性有機溶媒を用いた一態様を示すフローシートの概略図である。

1：フレツシュ1, 3-ブタジエンタンク、2：精製された回収溶剤タンク、3, 4：混合機、5：熟成槽、6：シス-1, 4重合反応槽、7：1, 2重合反応槽、8：補強ポリブタジエンゴム分離装置、9：補強ポリブタジエンゴム、10：二硫化炭素の吸着分離処理あるいは二硫化炭素付加物分離処理などの処理器、11：二硫化炭素、12：蒸留装置、13：高沸点物、20~39：導管、40：重合停止槽。

## 第 1 図

